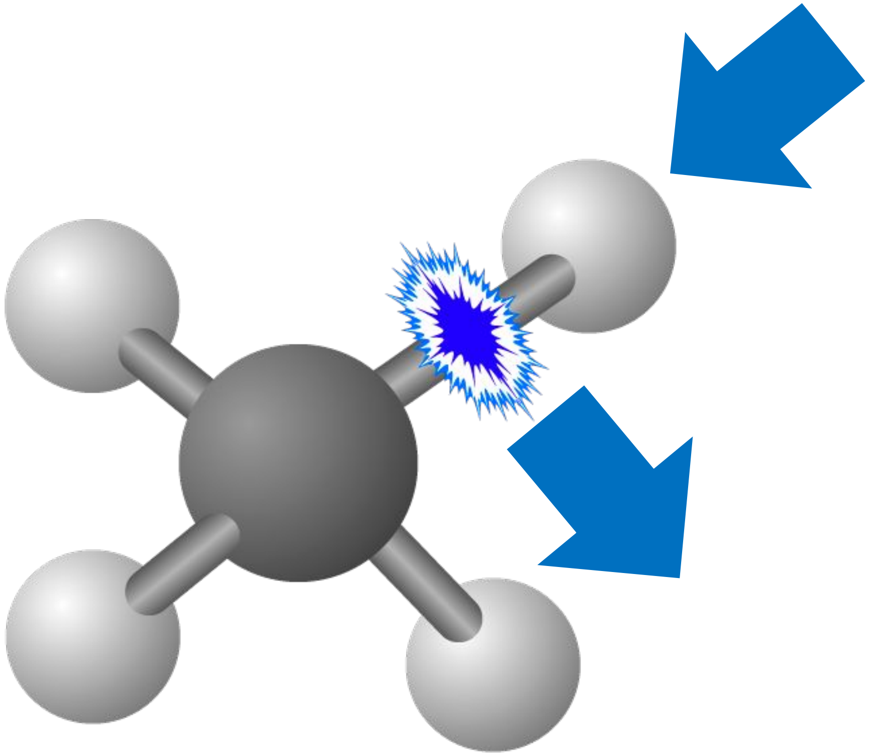
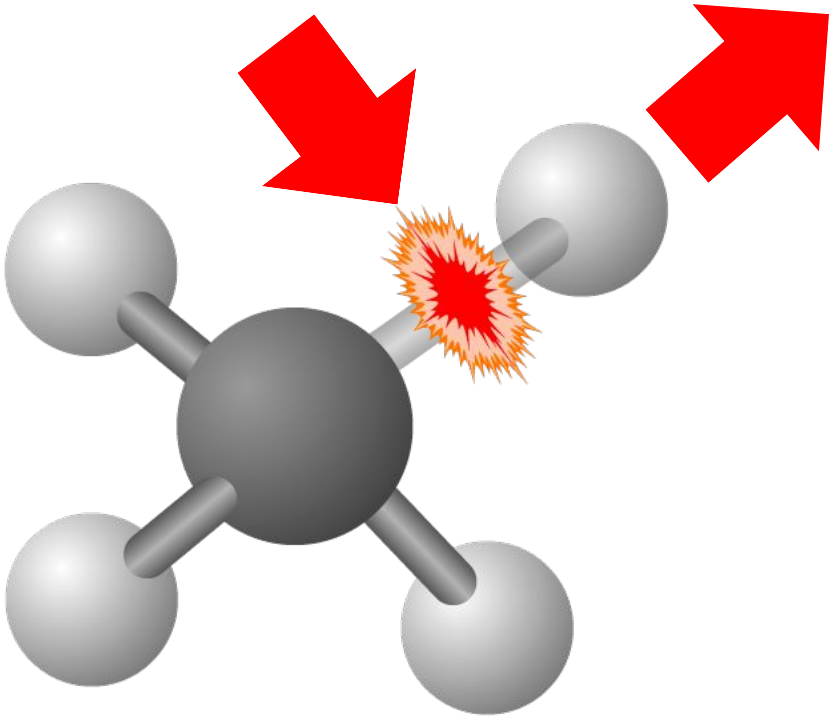
Energetics





Material Covered

Energetics

Edexcel

Students should:
Topic 13A: Lattice energy
1. be able to define lattice energy as the energy change when one mole of an ionic solid is formed from its gaseous ions
2. be able to define the terms: i enthalpy change of atomisation, $\Delta_{at}H$ ii electron affinity
3. be able to construct Born-Haber cycles and carry out related calculations
4. know that lattice energy provides a measure of ionic bond strength
5. understand that a comparison of the experimental lattice energy value (from a Born-Haber cycle) with the theoretical value (obtained from electrostatic theory) in a particular compound indicates the degree of covalent bonding
6. understand the meaning of polarisation as applied to ions
7. know that the polarising power of a cation depends on its radius and charge
8. know that the polarisability of an anion depends on its radius and charge
9. be able to define the terms 'enthalpy change of solution, $\Delta_{sol}H$', and 'enthalpy change of hydration, $\Delta_{hyd}H$'
10. be able to use energy cycles and energy level diagrams to carry out calculations involving enthalpy change of solution, enthalpy change of hydration and lattice energy
11. understand the effect of ionic charge and ionic radius on the values of: i lattice energy ii enthalpy change of hydration

AQA

3.1.8.1 Born–Haber cycles (A-level only)

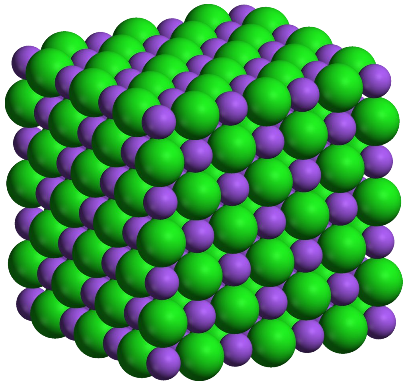
Content
Lattice enthalpy can be defined as either enthalpy of lattice dissociation or enthalpy of lattice formation. Born–Haber cycles are used to calculate lattice enthalpies using the following data: • enthalpy of formation • ionisation energy • enthalpy of atomisation • bond enthalpy • electron affinity. **Students should be able to:** • define each of the above terms and lattice enthalpy • construct Born–Haber cycles to calculate lattice enthalpies using these enthalpy changes • construct Born–Haber cycles to calculate one of the other enthalpy changes • compare lattice enthalpies from Born–Haber cycles with those from calculations based on a perfect ionic model to provide evidence for covalent character in ionic compounds. Cycles are used to calculate enthalpies of solution for ionic compounds from lattice enthalpies and enthalpies of hydration. **Students should be able to:** • define the term enthalpy of hydration • perform calculations of an enthalpy change using these cycles.

OCR

5.2.1 Lattice enthalpy

	Learning outcomes	Additional guidance
	Learners should be able to demonstrate and apply their knowledge and understanding of:	
Lattice enthalpy		
(a)	explanation of the term *lattice enthalpy* (formation of 1 mol of ionic lattice from gaseous ions, $\Delta_{LE}H$) and use as a measure of the strength of ionic bonding in a giant ionic lattice **(see also 2.2.2 b–c)**	Definition required.
Born–Haber and related enthalpy cycles		
(b)	use of the lattice enthalpy of a simple ionic solid (e.g. NaC*l*, MgC*l*$_2$) and relevant energy terms for: **(i)** the construction of Born–Haber cycles **(ii)** related calculations	*M2.2, M2.3, M2.4, M3.1* Relevant energy terms: *enthalpy change of formation, ionisation energy, enthalpy change of atomisation* and *electron affinity.* Definition required for first ionisation energy **(see also 3.1.1 c)** and enthalpy change of formation **(see also 3.2.1 d)** only. HSW2 Application of conservation of energy to determine enthalpy changes.
(c)	explanation and use of the terms: **(i)** *enthalpy change of solution* (dissolving of 1 mol of solute, $\Delta_{sol}H$) **(ii)** *enthalpy change of hydration* (dissolving of 1 mol of gaseous ions in water, $\Delta_{hyd}H$)	Definitions required. Details of infinite dilution **not** required.
(d)	use of the enthalpy change of solution of a simple ionic solid (e.g. NaC*l*, MgC*l*$_2$) and relevant energy terms (*enthalpy change of hydration* and *lattice enthalpy*) for: **(i)** the construction of enthalpy cycles **(ii)** related calculations	*M2.2, M2.3, M2.4, M3.1* HSW2 Application of conservation of energy to determine enthalpy changes.
(e)	qualitative explanation of the effect of ionic charge and ionic radius on the exothermic value of a lattice enthalpy and enthalpy change of hydration.	

Ionic Solids



Ionic solids contain a **metal** and a **non-metal** held together by **electrostatic attraction** between **oppositely charged ions**

Ionic solids can exist as **giant ionic lattices**, e.g. sodium chloride (NaCl)

Standard lattice enthalpy of formation, $\Delta_L H^\ominus$, is the **enthalpy change** when **one mole** of an **ionic lattice** is **formed** from its **gaseous ions** under **standard conditions**

$\Delta_L H^\ominus = -788\ \text{kJ mol}^{-1}$

As **new bonds** are **formed** and **energy is released** in the **formation of a lattice**, it is an **exothermic** reaction, so $\Delta_L H^\ominus$ is **always negative**

Ionic Solids

$\Delta_L H^\ominus$ is **dependent** on the **strength** of the **ionic bonds** formed, and therefore, the **size** and **charge** of the **ions** involved

$\mathbf{\Delta_L H^\ominus}$ will be **larger** when:

	Larger charge density and **smaller ionic radii** allows for ions to **sit closer** together so **ionic bonds** are **stronger**
	The **more highly charged** the ions the **stronger** the **ionic bonds** and so **more energy** is **released** on formation

Ionic Solids

$\Delta_L H^{\ominus}$ NaCl = -717 kJ mol^{-1}

$\Delta_L H^{\ominus}$ $MgCl_2$ = -2526 kJ mol^{-1}

$\Delta_L H^{\ominus}$ MgS = -3299 kJ mol^{-1}

							1 H										4 He
7 Li	9 Be											11 B	12 C	14 N	16 O	19 F	20 Ne
23 Na	24 Mg											27 Al	28 Si	31 P	32 S	35.5 Cl	40 Ar
39 K	40 Ca	45 Sc	48 Ti	51 V	52 Cr	55 Mn	56 Fe	59 Co	59 Ni	63.5 Cu	65 Zn	70 Ga	73 Ge	75 As	79 Se	80 Br	40 Ca
85 Rb	88 Sr	89 Y	91 Zr	93 Nb	96 Mo	[98] Tc	101 Ru	103 Rh	106 Pd	108 Ag	112 Cd	115 In	119 Sn	122 Sb	128 Te	127 I	131 Xe
133 Cs	137 Ba	139 La*	178 Hf	181 Ta	184 W	186 Re	190 Oscv	192 Ir	195 Pt	197 Au	201 Hg	204 Tl	207 Pb	[209 Bi	[209] Po	[210] At	[222] Rn
[223] Fr	[226] Ra	[227] Ac*															

Mg^{2+} has a **smaller ionic radius** than Na^+ and is **doubly charged**, therefore $\Delta_L H^{\ominus}$ $MgCl_2$ is **more negative** than $\Delta_L H^{\ominus}$ NaCl

S^{2-} and Cl^- have roughly the **same ionic radius**, but $\Delta_L H^{\ominus}$ MgCl transfers the **most** energy because both Mg^{2+} and S^{2-} are both **doubly charged**

Standard enthalpy of atomisation is the **enthalpy change** when **one mole of gaseous atoms** form **from the element** in its **standard state** under **standard conditions**

Standard ionisation energy (IE) is the **enthalpy change** when **one mole of electrons** is **removed** from **one mole of gaseous atoms** under **standard conditions**

Standard electron affinity is the **enthalpy change** when **one mole of electrons** is **added** to **a mole of gaseous atoms** under **standard conditions**

Standard enthalpy of formation is the **enthalpy change** when **one mole** of a substance is **formed** from its **constituent elements** in their **standard states**, under **standard conditions**

Exemplar Exam Question – Statement + Short Answer

1) a) Define “lattice enthalpy of formation”.

[1 mark]

Command: simple recall of definition

Direction: lattice enthalpy of formation

Context: formation of ionic solids

Exemplar Exam Question – Statement + Short Answer

1) b) Explain the factors that affect the magnitude of the lattice enthalpy of formation of an ionic solid.

[2 marks]

Command: more detailed response, critical thought required

Direction: state the factors and explain how it links to the magnitude of $\Delta_L H^\ominus$

Context: factors affecting $\Delta_L H^\ominus$

Exemplar Exam Question – Statement + Short Answer

1) a) Define “lattice enthalpy of formation”.

[1 mark]

Lattice enthalpy of formation, $\Delta_L H^{\ominus}$, is the enthalpy change when one mole of an ionic solid is formed from its gaseous ions under standard conditions.

Exemplar Exam Question – Statement + Short Answer

1) b) Explain the factors that affect the magnitude of the lattice enthalpy of formation of an ionic solid.

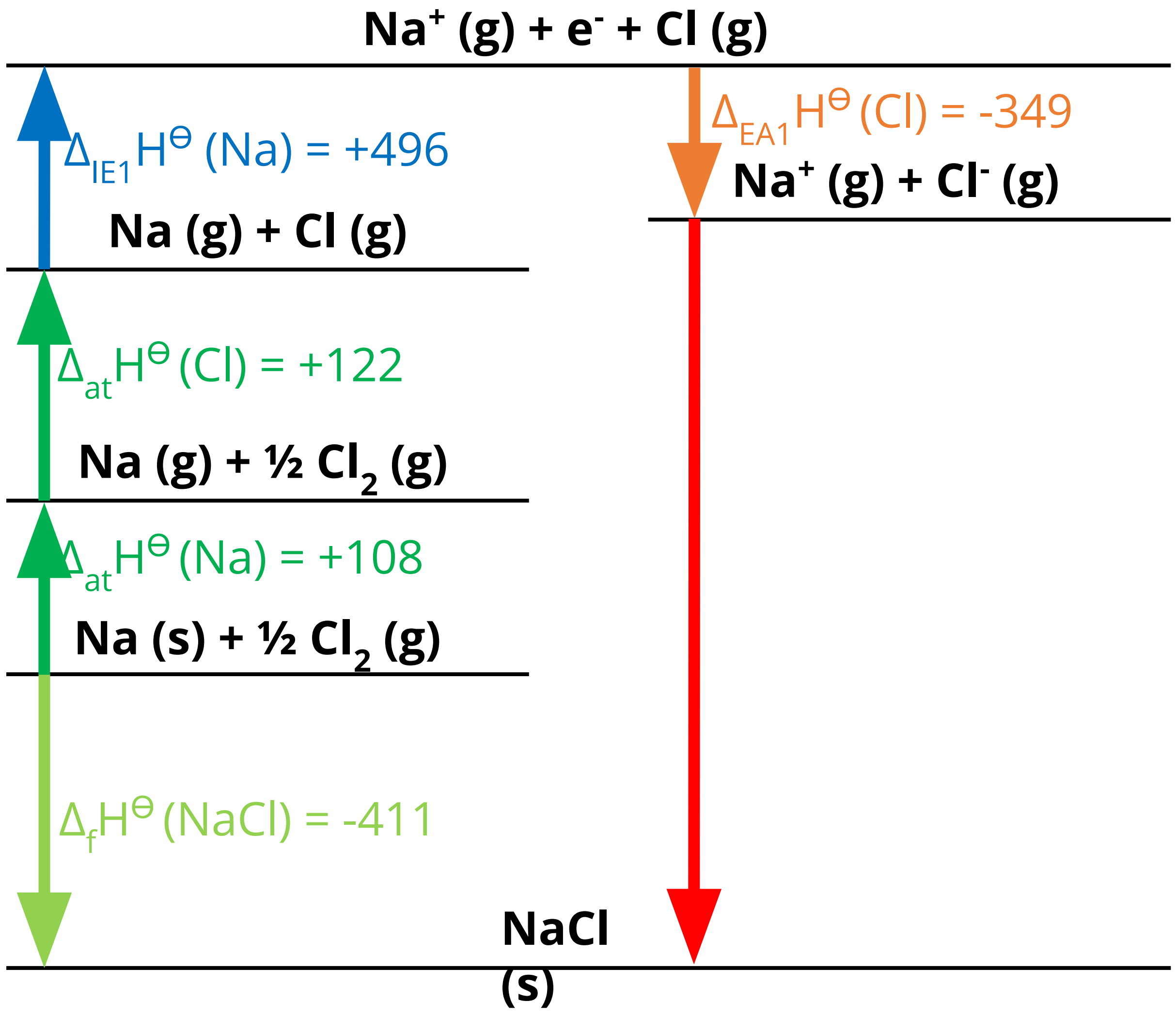
[2 marks]

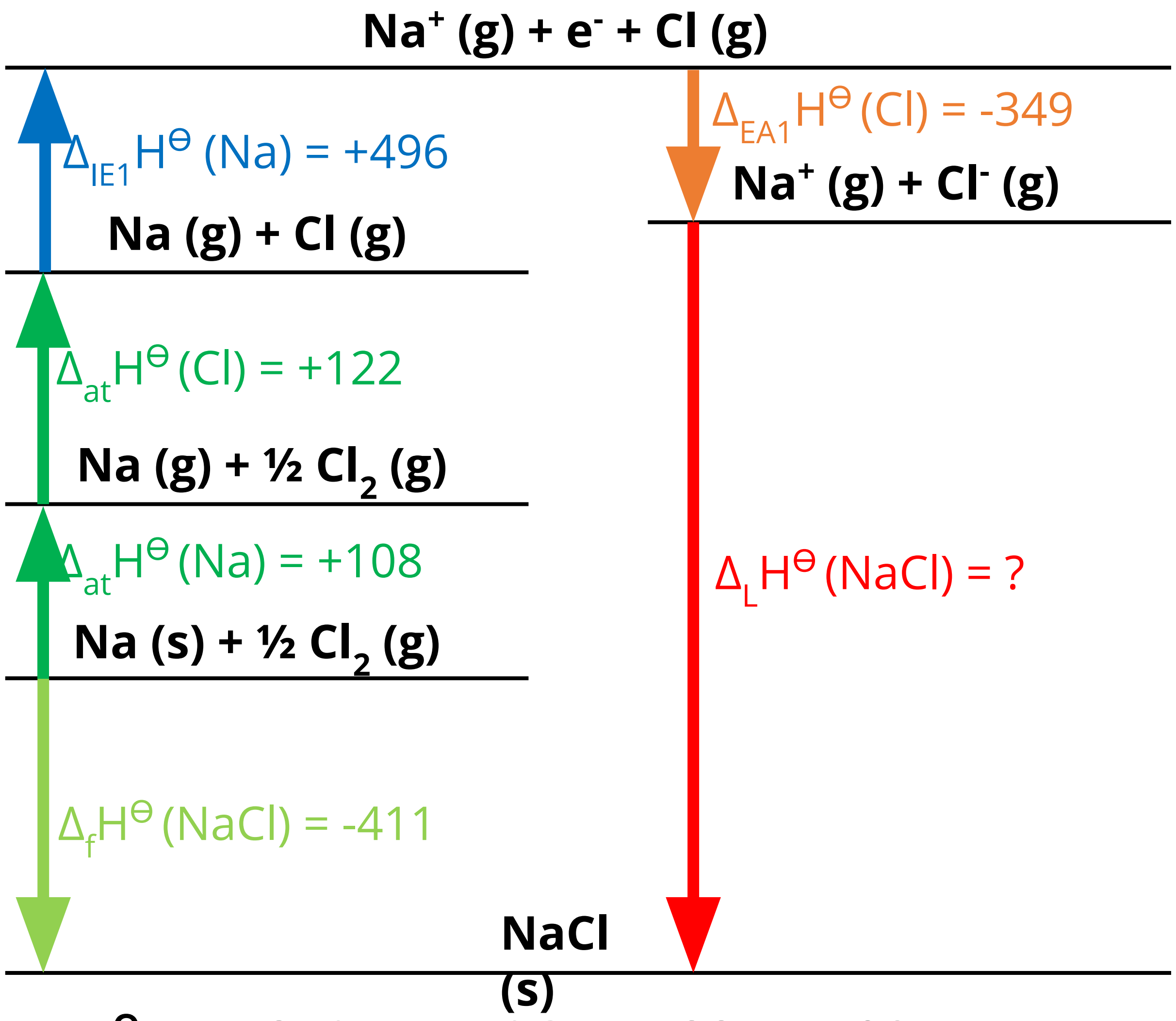
Ionic charge can affect $\Delta_L H^{\ominus}$ – the more highly charged the ion, the stronger the ionic bonds and so more energy is released in the formation of an ionic lattice. Ionic radius can also affect $\Delta_L H^{\ominus}$ – the smaller the ionic radius, the larger the charge density and the closer the ions can sit together. This makes the ionic bonds stronger and the lattice enthalpy larger.

Born-Haber Cycles

Hess' law states the **enthalpy change** for a chemical reaction is the **same**, **whatever route** is taken from reactants to products

Lattice enthalpies are **impossible** to **measure directly** because it's **difficult** to **prepare** the **right amount of gaseous ions** and **measure** the **energy change** as they **form exactly a mole** of the **ionic solid** – so we use





$\Delta_{LE}H^⊖ = – (-349) – (+496) – (122) – (108) + (-411)$

1. Start with **elements** in their **standard states**
2. Add $\Delta_f H^⊖$ (**negative** so the arrow points **downwards**)- form NaCl
3. Add $\Delta_{at}H^⊖$ **(Na)** from the elements in their standard states - form Na (g) from Na (s)
4. Add $\Delta_{at}H^⊖$ **(Cl)** - form Cl (g) from Cl (s)
5. Add $\Delta_{IE1}H^⊖$ **(Na)**
6. Add $\Delta_{EA1}H^⊖$ **(Cl)** (**negative** so the arrow points **downwards**)
7. Calculate $\Delta_{LE}H^⊖$ **(NaCl)** – we know this is **exothermic** so arrow points **downwards**

-ve (exothermic) enthalpies point **downwards**
+ve (endothermic) enthalpies point **upwards**

Exemplar Exam Question – Calculation

2) The Born-Haber cycle of CaF is shown with all enthalpy values given in kJ mol^{-1}.

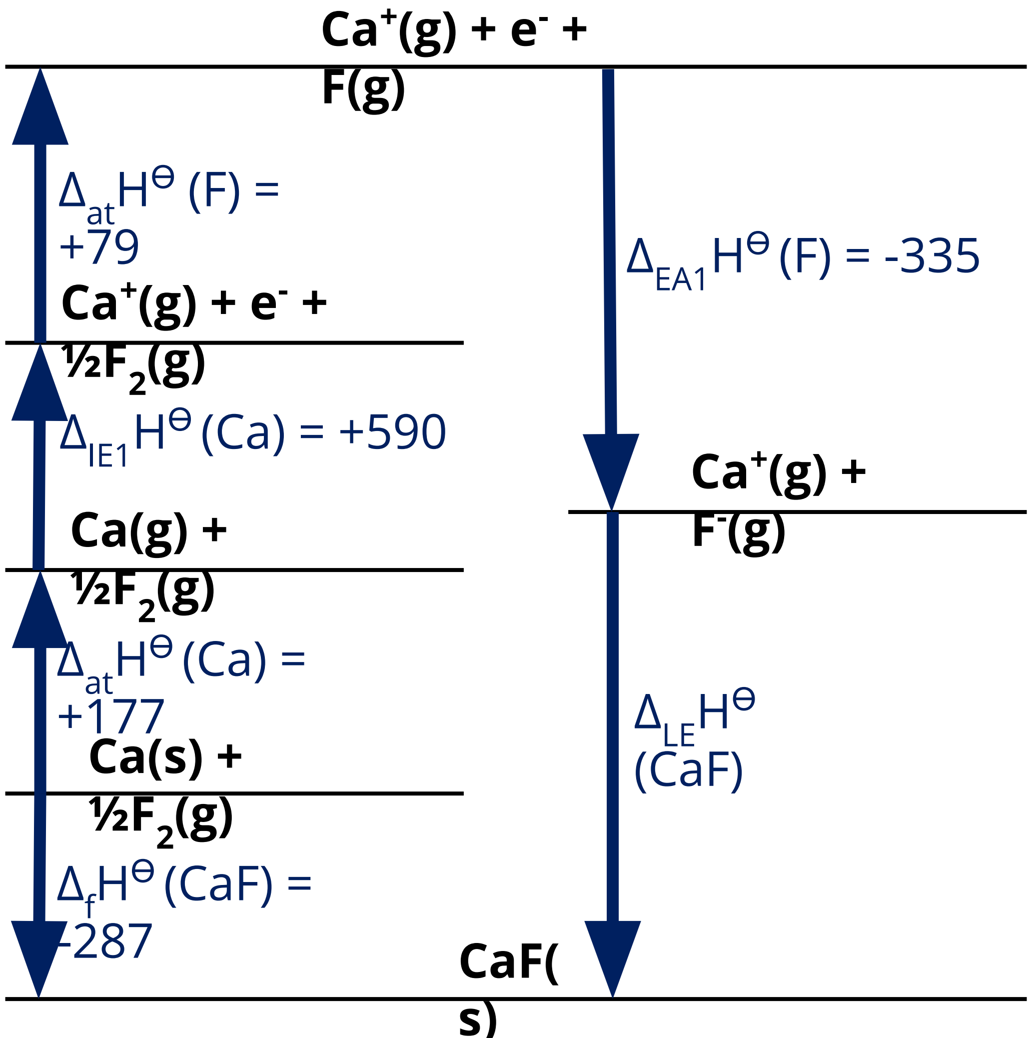
Calculate the lattice enthalpy of formation of calcium fluoride.

[2 marks]

Command: show your full working

Context: Born-Haber cycle calculations

Direction: work out $\Delta_L H^\ominus$ using the numbers in the cycle



Exemplar Exam Question – Calculation

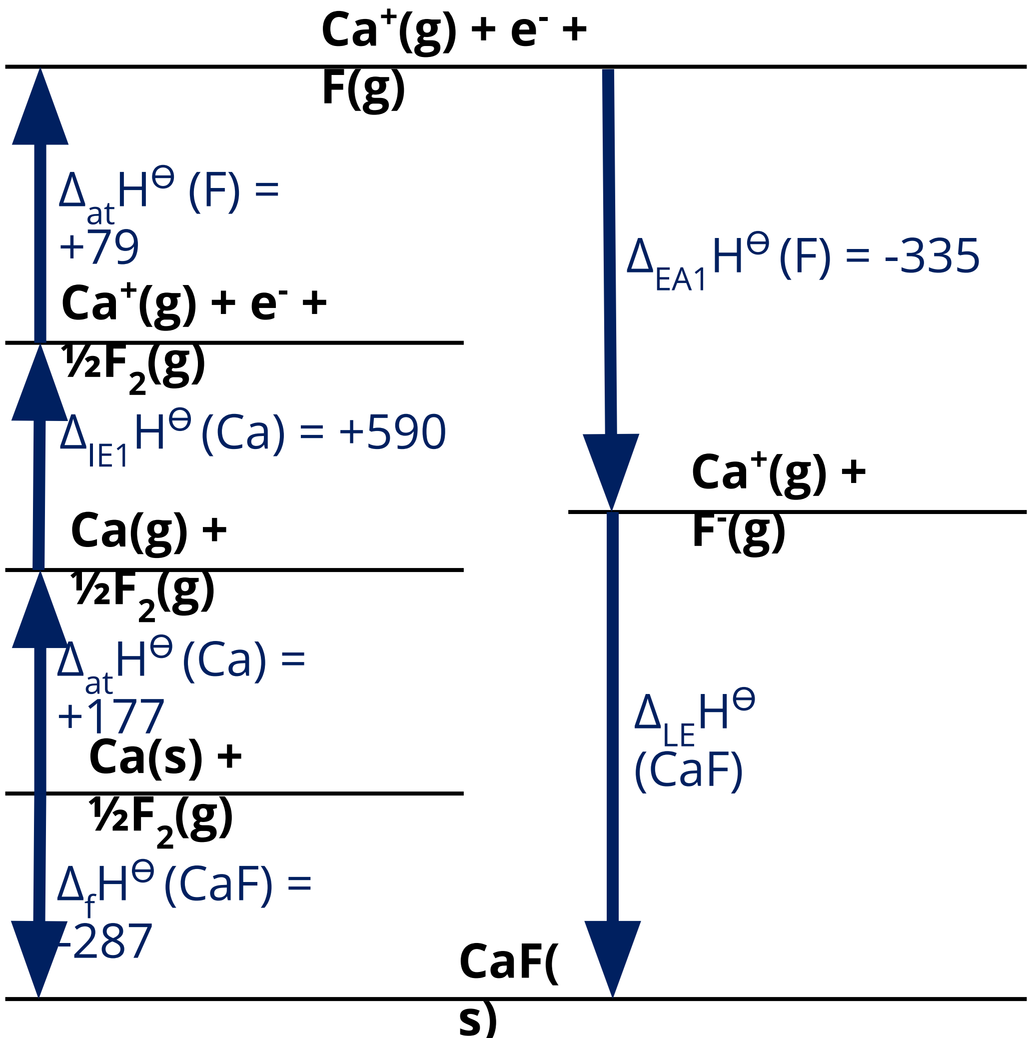
2) The Born-Haber cycle of CaF is shown with all enthalpy values given in kJ mol^{-1}.

Calculate the lattice enthalpy of formation of calcium fluoride.

[2 marks]

CORRECTION: The compound CaF can't exist, although the maths given is correct.

See the mini mock paper for the Born-Haber cycle of the correct compound CaF_2

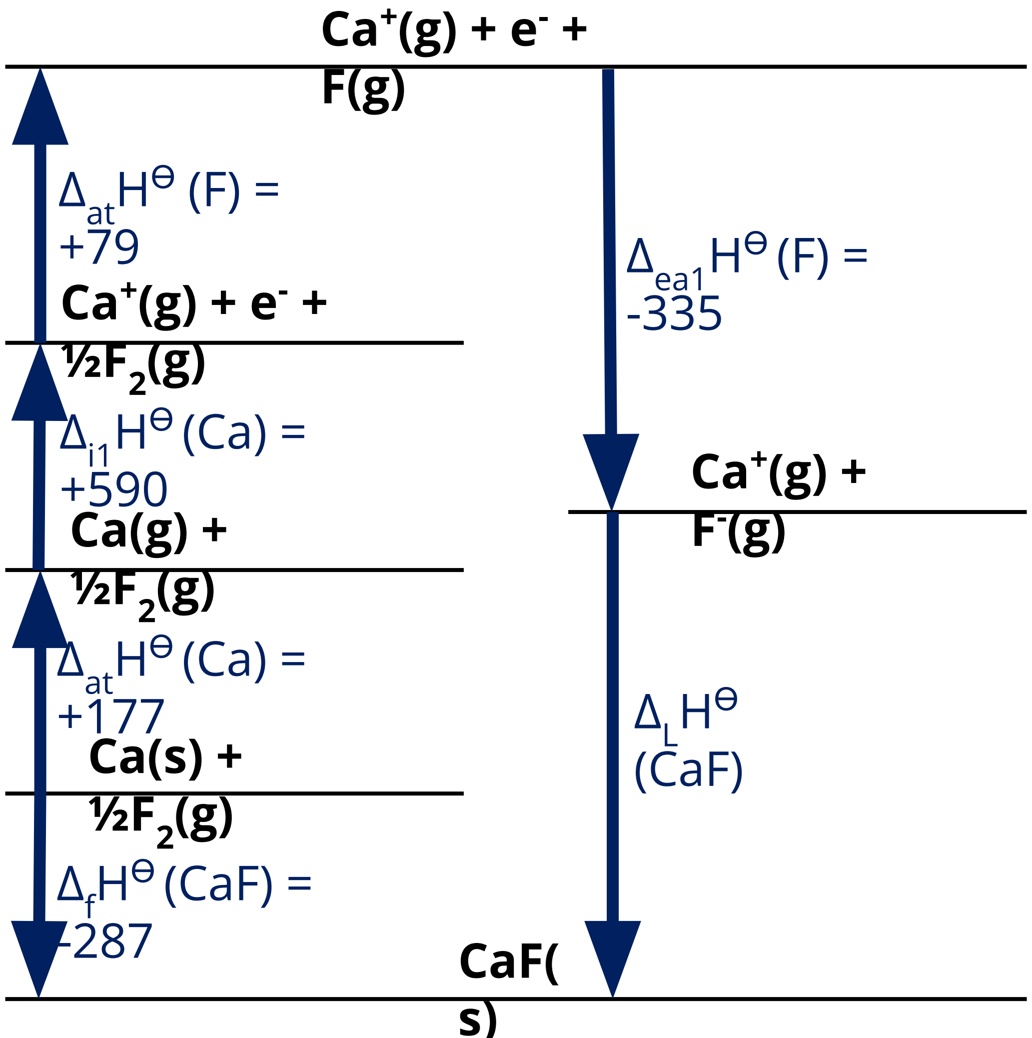


Exemplar Exam Question – Calculation

2) The Born-Haber cycle of CaF is shown with all enthalpy values given in kJ mol^{-1}.

Calculate the lattice enthalpy of formation of calcium fluoride.

[2 marks]



$\Delta_{LE}H^\ominus$ (CaF) = – (-335) – (+79) – (+590) – (+177) + (-287)

= -798 kJ mol^{-1}

Not in OCR specification

Assumptions in ionic bonding

Ions are in **contact** with each other

Ions are perfectly **spherical**

Charge of each ion is **evenly distributed** in space

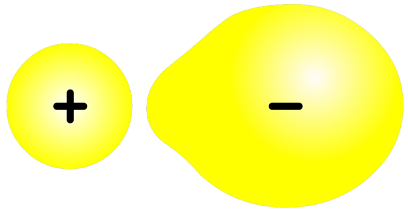
Polarisation

Not in OCR specification

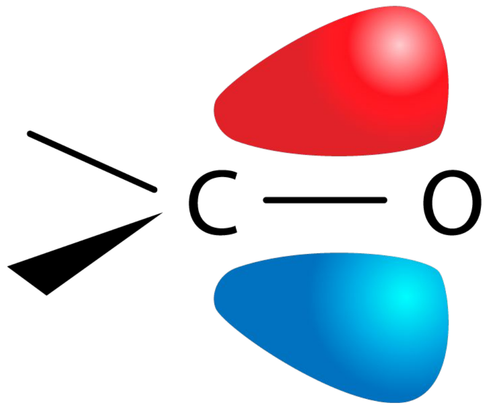
There is a **continuum** between **ionic bonding** and **covalent bonding** – **ionic solids** may **not only have ionic bonding**, but

Covalent character arises due to

Polarisation is **distortion** of **electron density** which leads to **more electrons** being present between the **nuclei** and an

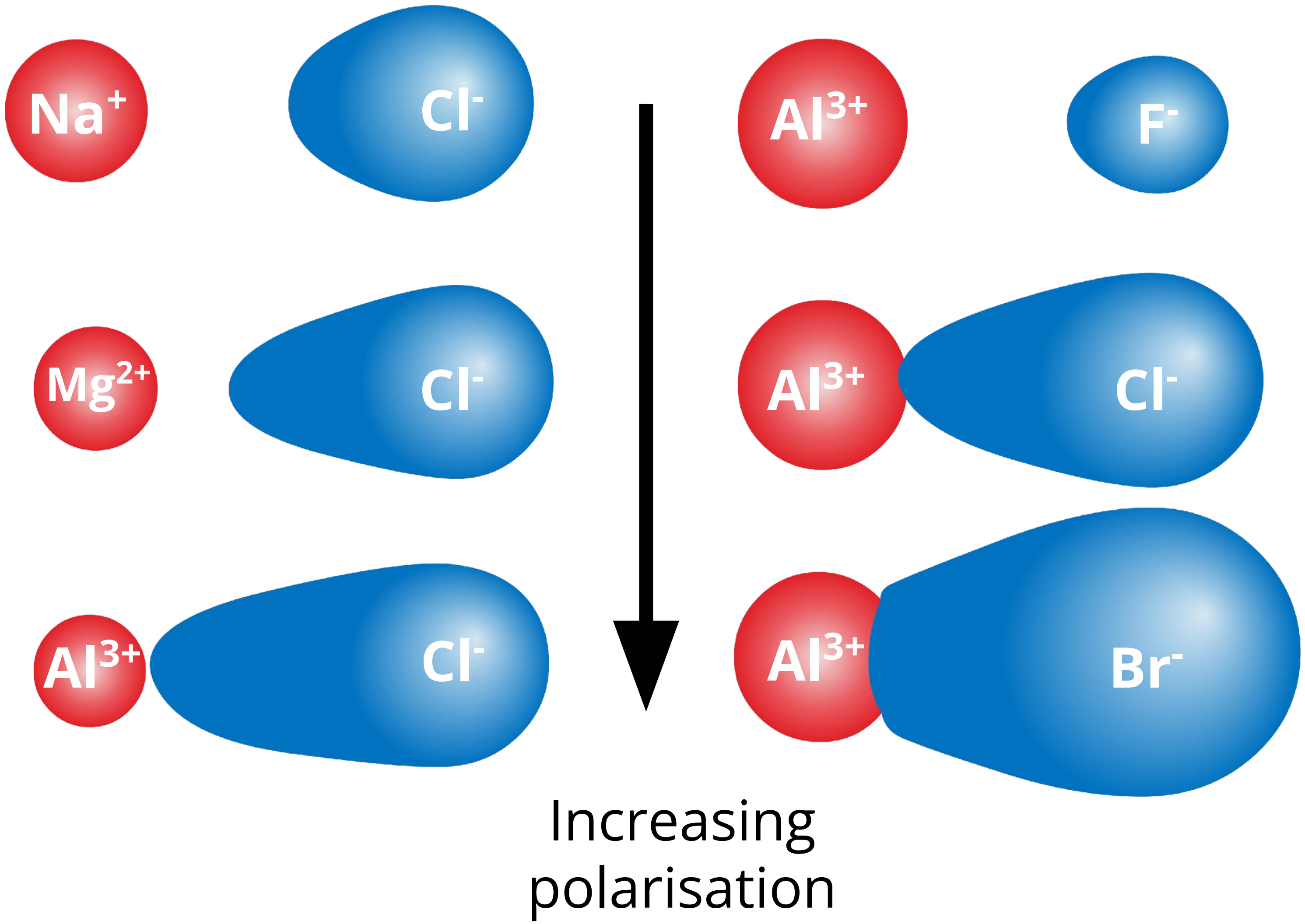


Polarisation arises when a **small**, **highly positive cation** causes a **distortion** of the **electrons** in a **large**, **highly negative anion**



Polarisation

Not in OCR specification



Polarisation

Not in OCR specification

Discrepancies between **experimental values** (from **Born-Haber cycles**) and **theoretical values** (from the **perfect ionic model**) indicates the **degree of covalent bonding** in an **ionic solid**

The **theoretical value** assumes **purely ionic bonds**, but **polarisation** causes **covalent character** in **ionic bonds**, making the **bonding stronger** and the lattice enthalpy **more negative** (**more exothermic**)

Exemplar Exam Question – Long Answer

3) Explain how and why the experimental value of the lattice enthalpy of silver chloride differs from the theoretical value.

[4 marks]

Command: more detailed response, how do they differ and why

Direction: compare experimental and theoretical and give reasoning as to why we see this difference

Context: experimental lattice enthalpies vs. theoretical lattice enthalpies

Exemplar Exam Question – Long Answer

3) Explain how and why the experimental value of the lattice enthalpy of silver chloride differs from the theoretical value.

[4 marks]

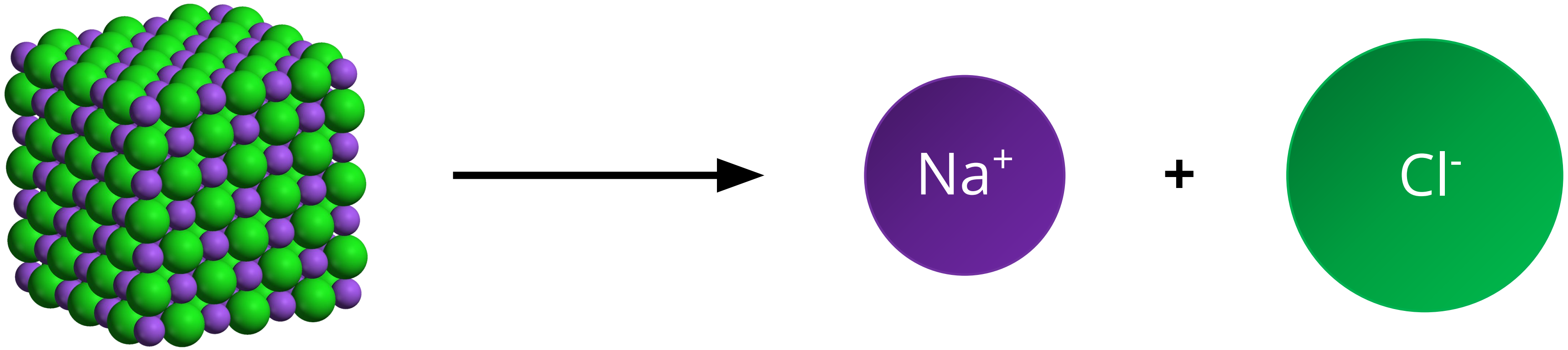
Discrepancies between the experimental and theoretical values may arise due to covalent character. Theoretical values assume purely ionic bonding, whereas experimental values may have some degree of covalent bonding. Polarisation causes covalent character in ionic bonds, making the bonding stronger and the lattice enthalpy of AgCl larger. The greater the discrepancy the greater the degree of covalent bonding involved.

Enthalpies of Solution

The first step of **dissolving** a lattice **requires energy**

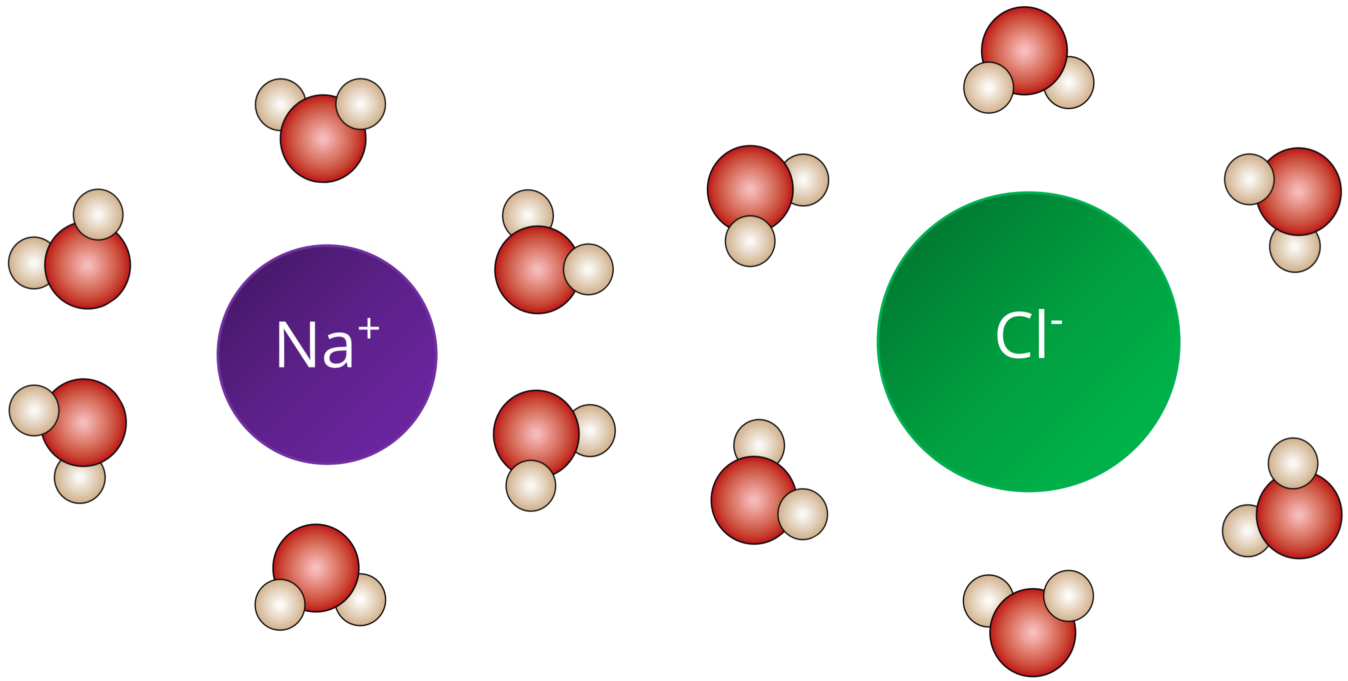
It is the **reverse** of the **lattice enthalpy of formation** – it has the **same value** but it is **always positive** (**endothermic**) because **bonds** are **broken**

Standard lattice enthalpy of dissociation, $\Delta_{LE}H^{\ominus}$ (+ve), is the **enthalpy change** when **one mole** of an **ionic lattice dissociates** into its **gaseous ions**, e.g. NaCl (s) □ Na^+ (g) + Cl^- (g)



Enthalpies of Solution

Once dissociated, the **separate ions** can be **solvated**, usually by **water**. Water **clusters** around the ions so that the **-ve** end of the **dipole surround** the **+ve ions**, and the **+ve** end of the **dipole surround** the **-ve ions**



Standard enthalpy of hydration, $\Delta_{hyd}H^{\ominus}$, is the **enthalpy change** when **water molecules** surround **one mole** of **gaseous ions under standard conditions**

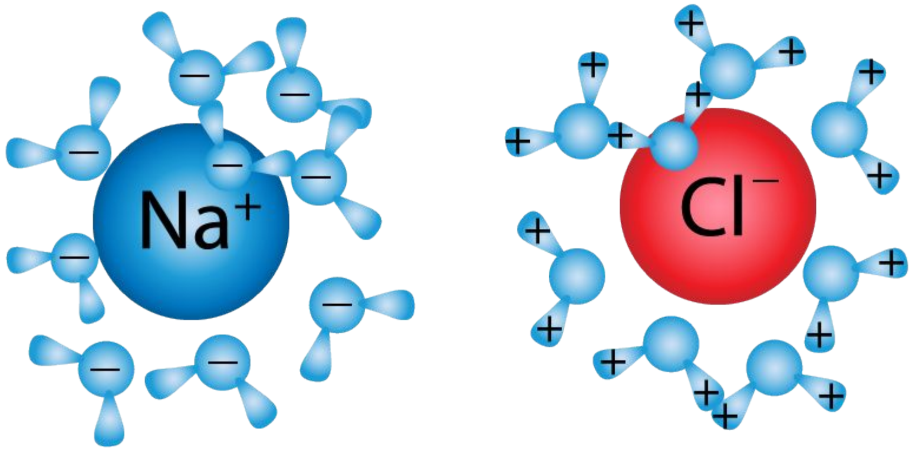
e.g. Na^{+} (g) + aq □ Na^{+} (aq)

Standard enthalpy of solution, $\Delta_{sol}H^{\ominus}$, is the **enthalpy change** when **one mole** of **solute dissolves completely** in **sufficient solvent under standard conditions** forming a **solution** where **molecules/ions do not interact** with each other

e.g. NaCl (s) + aq □ Na^{+} (aq) + Cl^{-} (aq)

$\Delta_{hyd}H^{\ominus}$ follows the **same trend** as the **lattice enthalpy of formation** – it will be **more negative** and therefore **give out more energy** with:

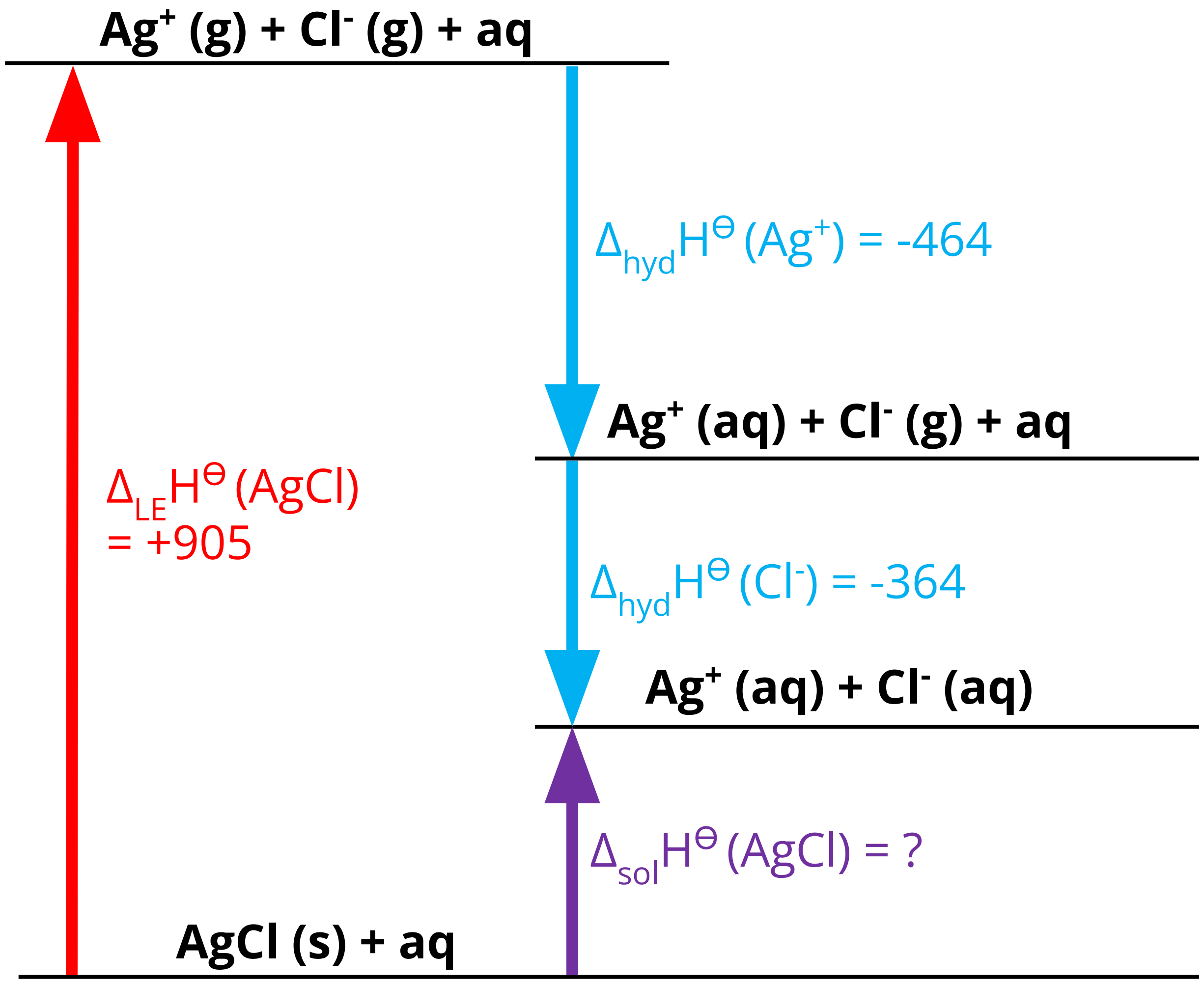
-
-



We can use **Born-Haber cycles** to calculate $\mathbf{\Delta_{sol}H^{\ominus}}$. For example, if we wish to calculate $\mathbf{\Delta_{sol}H^{\ominus}}$ **(AgCl)**

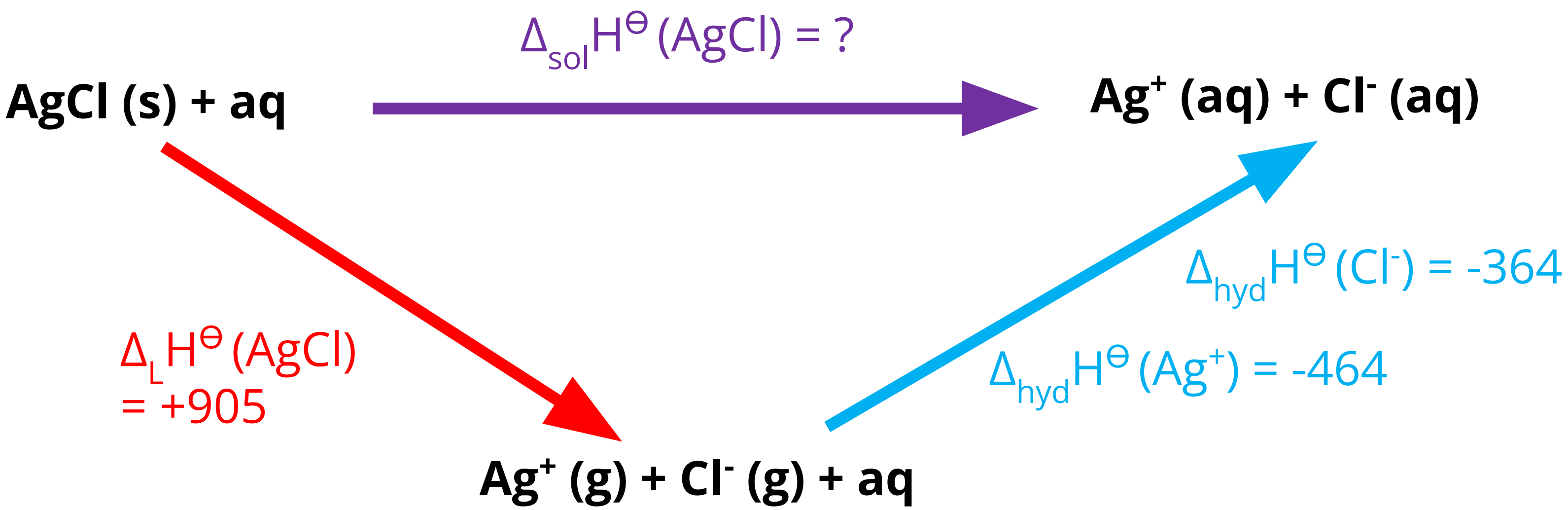
1. Start at the **bottom** with the **solid ionic lattice** and add $\mathbf{\Delta_{sol}H^{\ominus}}$ **(AgCl)** pointing **upwards**
2. Add $\mathbf{\Delta_{LE}H^{\ominus}}$ **(AgCl)** – make sure the **arrow points the right way** depending on whether the value is **positive or negative**
3. Add $\mathbf{\Delta_{hyd}H^{\ominus}}$ $\mathbf{(Ag^{+})}$
4. Add $\mathbf{\Delta_{hyd}H^{\ominus}}$ $\mathbf{(Cl^{-})}$
5. Calculate $\mathbf{\Delta_{sol}H^{\ominus}}$ **(AgCl)**

$$\Delta_{sol}H^{\ominus}(AgCl) = (+905) + (-464) + (-364)$$



Enthalpies of Solution

Alternatively, we can draw a **Hess cycle** to calculate the **enthalpy of solution** – it will give the **same answer**



$$\Delta_{sol}H^{\ominus}(AgCl) = (+905) + (-464) + (-364)$$

Exemplar Exam Question – Statement + Calculation

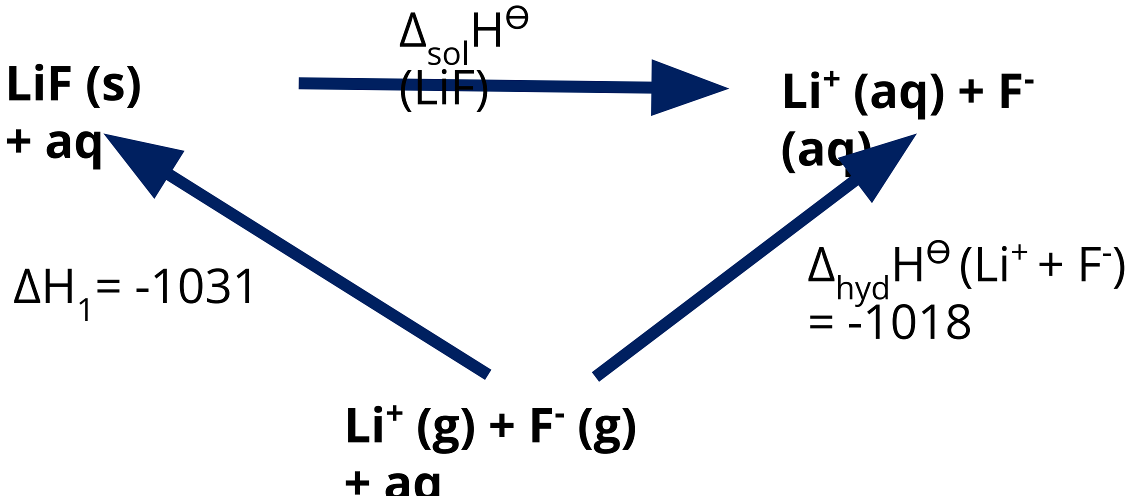
4) A Hess cycle can be drawn to calculate the enthalpy of solution of lithium fluoride.

a) State the type of enthalpy change represented by ΔH_1.
[1 mark]

Command: simple recall

Context: Hess cycles and their labels

Direction: Asked to name the arrow that points up from gaseous elements to ionic solid



Exemplar Exam Question – Statement + Calculation

4) A Hess cycle can be drawn to calculate the enthalpy of solution of lithium fluoride.

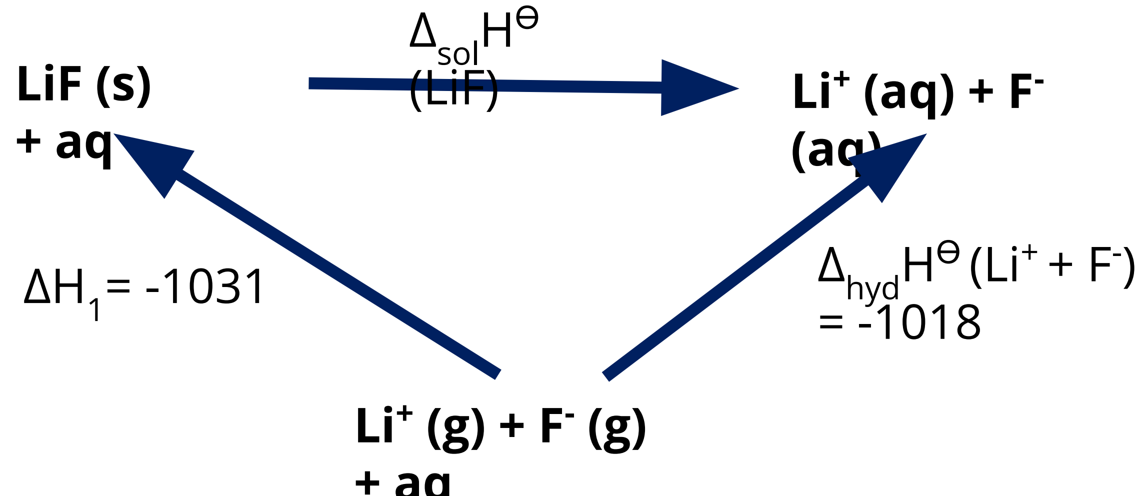
b) Calculate the enthalpy of solution of lithium fluoride using the data provided (all values are in kJ mol^{-1}).

[2 marks]

Command: show your full working

Direction: use the Hess cycle to calculate $\Delta_{sol}H^{\ominus}$ in kJ mol^{-1}

Context: calculating $\Delta_{sol}H^{\ominus}$ using Hess cycles



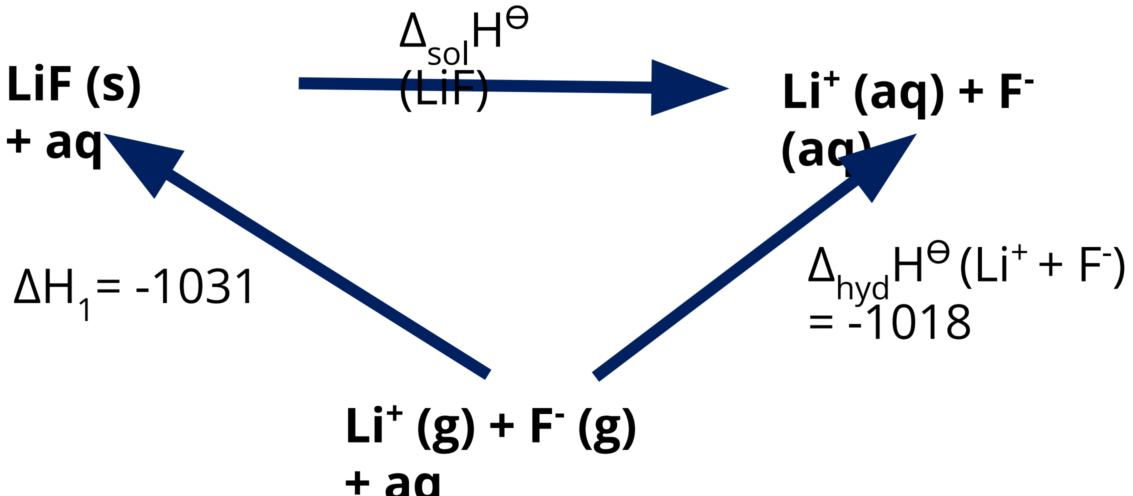
Exemplar Exam Question – Statement + Calculation

4) A Hess cycle can be drawn to calculate the enthalpy of solution of lithium fluoride.

a) State the type of enthalpy change represented by ΔH_1.

[1 mark]

ΔH_1 = lattice enthalpy of formation of lithium fluoride



Exemplar Exam Question – Statement + Calculation

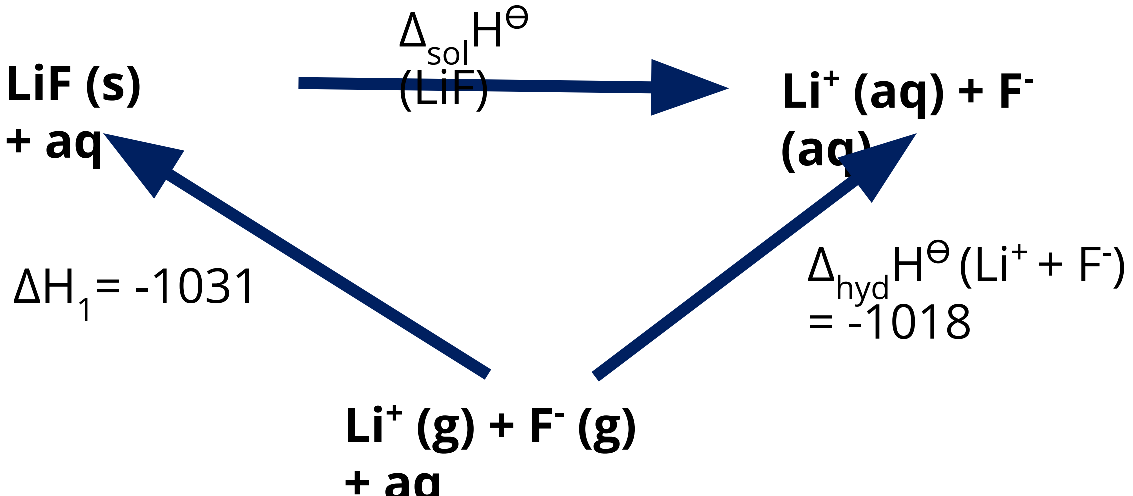
4) A Hess cycle can be drawn to calculate the enthalpy of solution of lithium fluoride.

b) Calculate the enthalpy of solution of lithium fluoride using the data provided (all values are in kJ mol^{-1}).

[2 marks]

$\Delta_{sol}H^{\ominus}$ (LiF) = - (-1031) + (-1018)

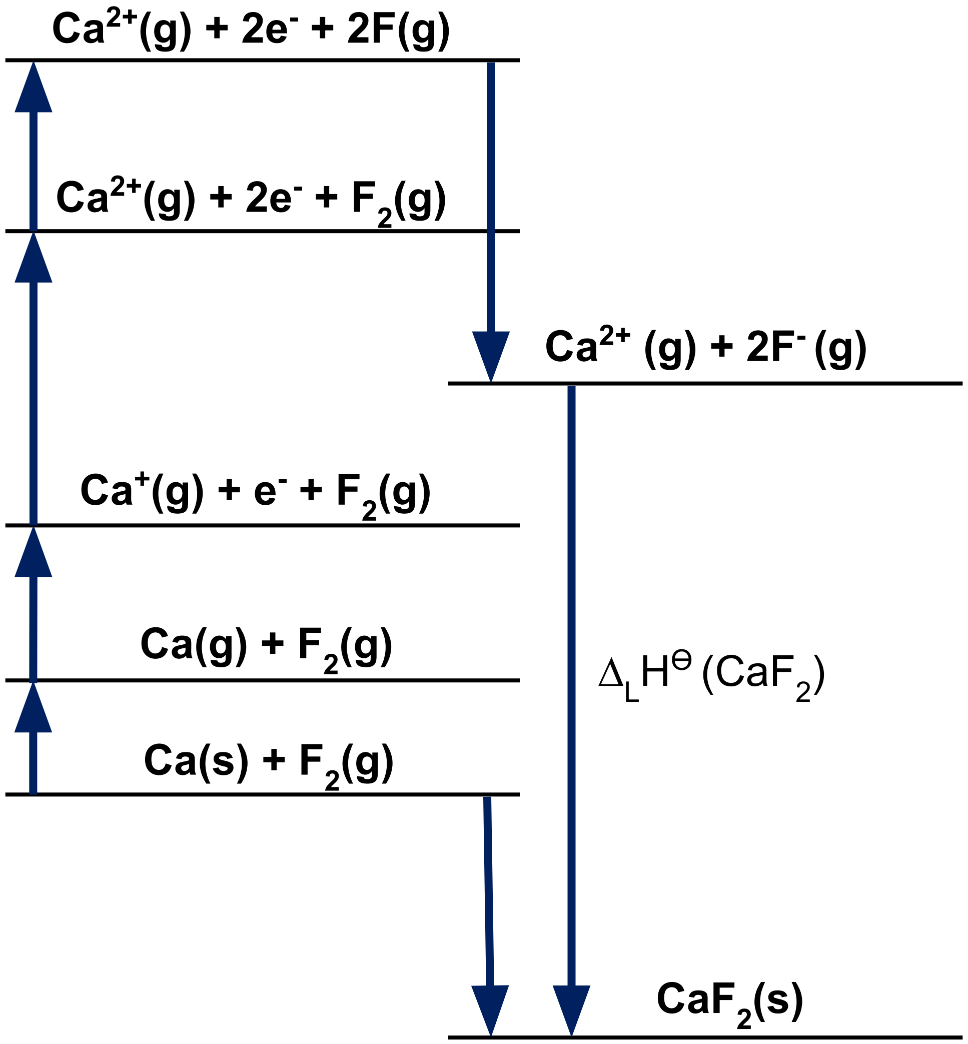
= +13 kJ mol^{-1}



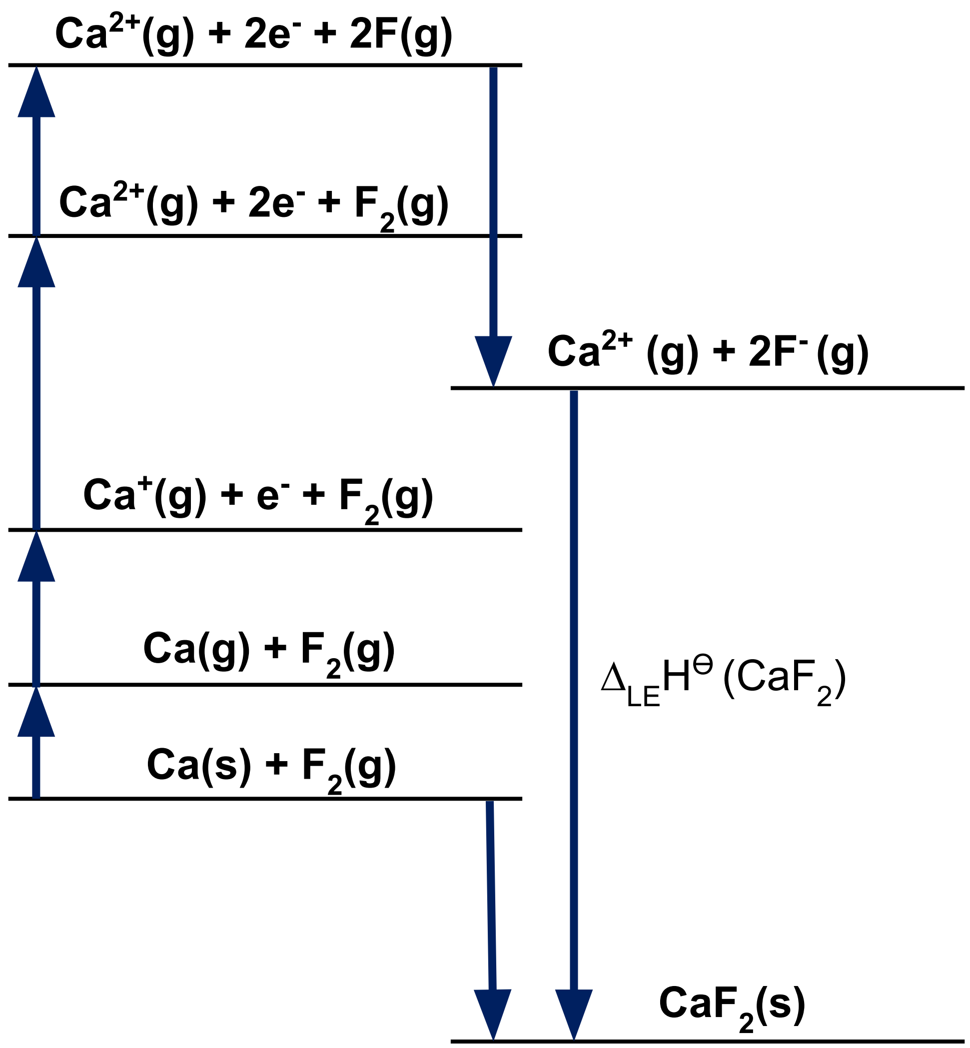
Mini Mock Paper

1a) Complete and label the Born-Haber cycle for the formation of calcium fluoride using the data provided. **[3 marks]**

Process	Enthalpy change / kJ mol^{-1}
First ionisation energy of calcium	+590
Second ionisation energy of calcium	+1140
Electron affinity of fluorine	-335
Enthalpy change of formation for calcium fluoride	-1185
Enthalpy change of atomisation for calcium	+177
Enthalpy change of atomisation for fluorine	+79

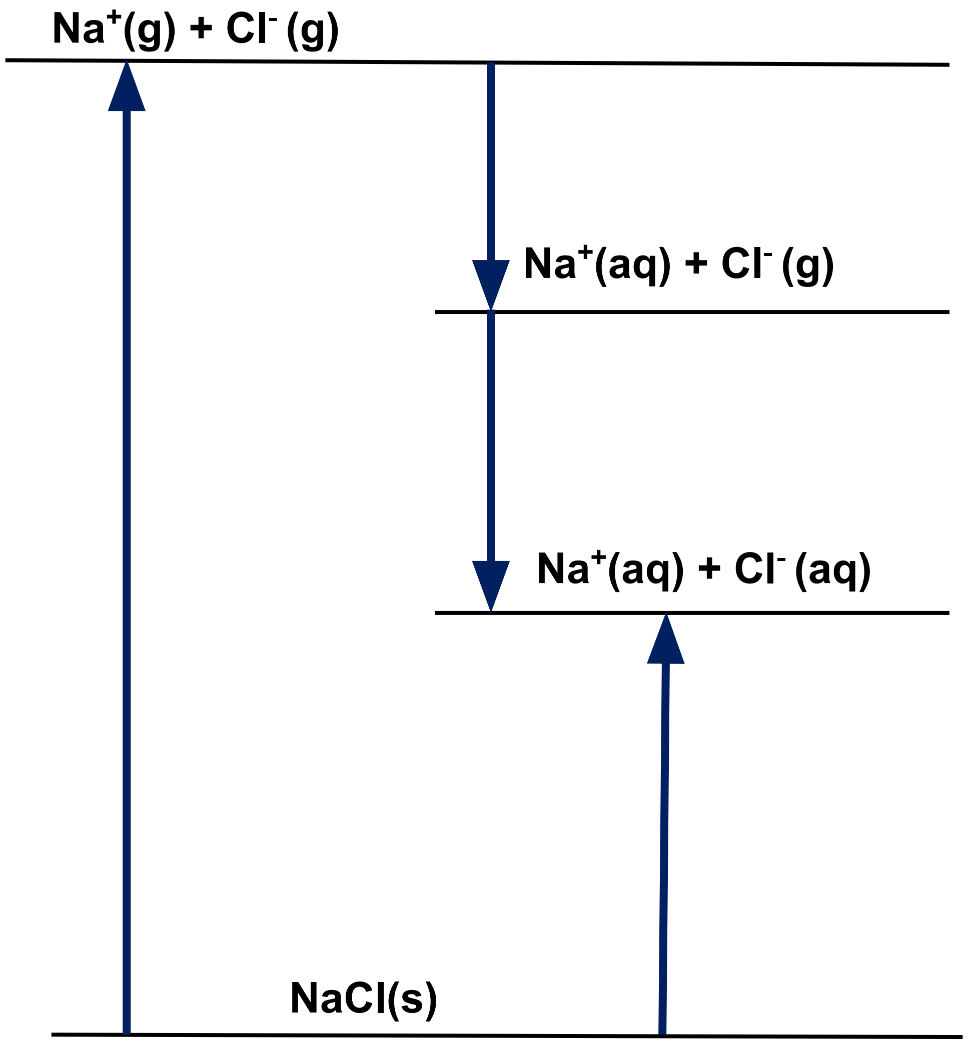


1b) Using your completed diagram, calculate the lattice enthalpy of formation of calcium fluoride. **[2 marks]**

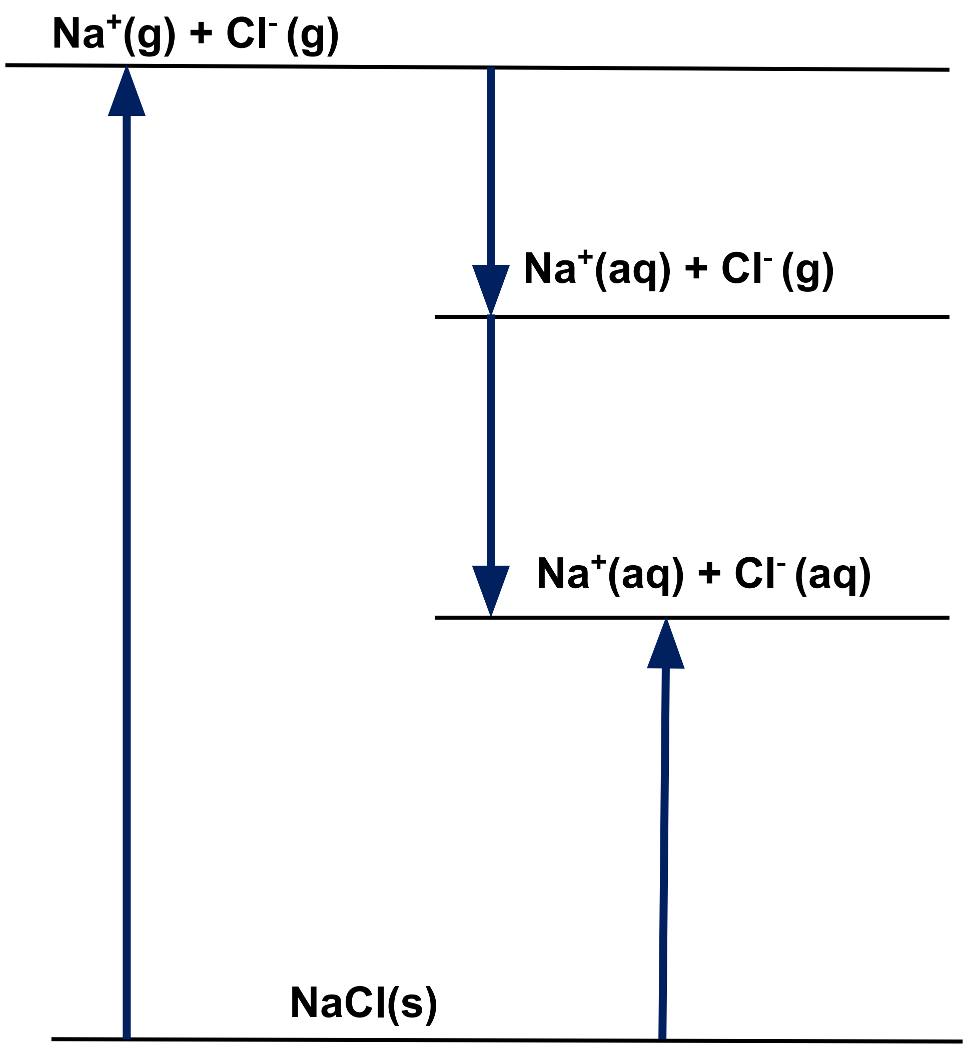


2a) Complete and label the solvation enthalpy cycle for the solvation of sodium chloride using the data provided. **[4 marks]**

Process	Enthalpy change / kJ mol^{-1}
Lattice Enthalpy of NaCl	+788
Enthalpy of hydration of Cl^-	-406
Enthalpy of hydration of Na^+	-363



2b) Using your completed diagram, calculate enthalpy of solvation for sodium chloride.
[2 marks]



Mini Mock Paper Answers

1a) Label the Born-Haber cycle for the formation of calcium fluoride using the data provided. **[3 marks]**

Process	Enthalpy change / kJ mol^{-1}
First ionisation energy of calcium	+590
Second ionisation energy of calcium	+1140
Electron affinity of fluorine	-335
Enthalpy change of formation for calcium fluoride	-1185
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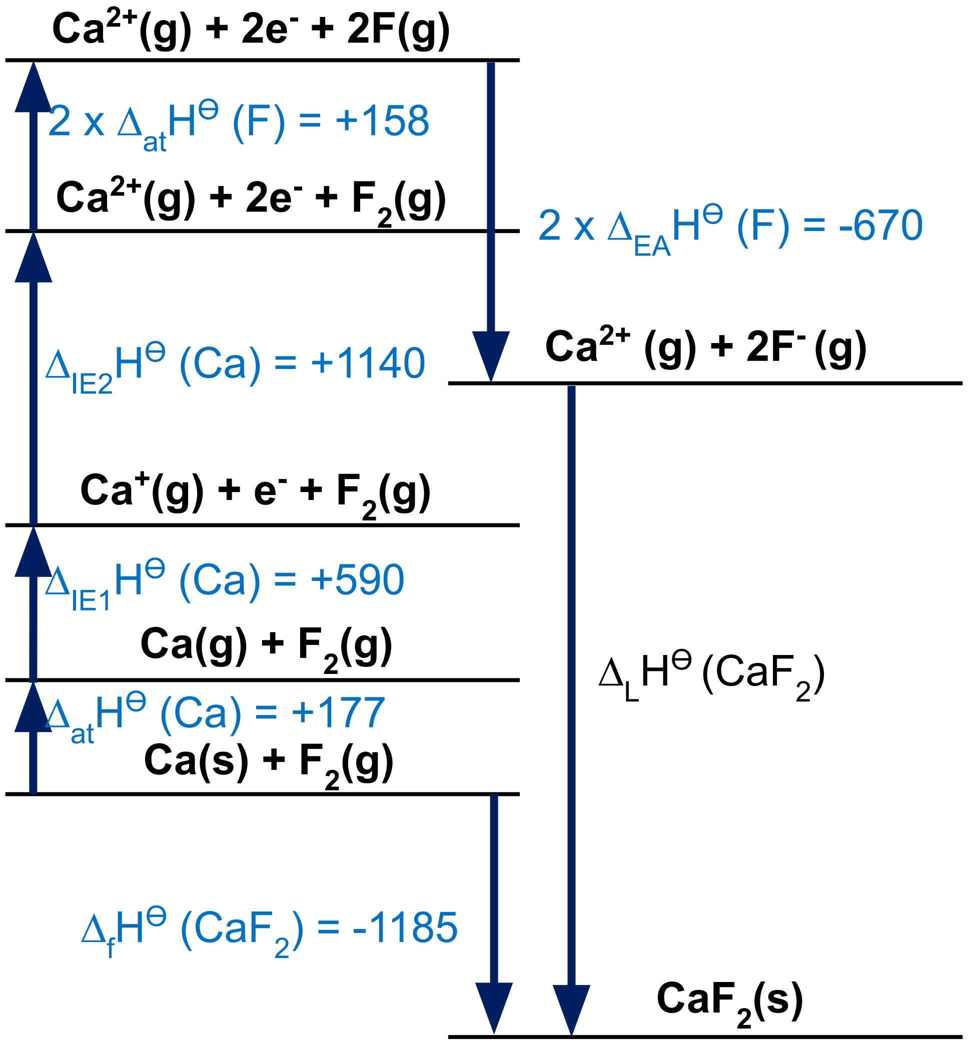
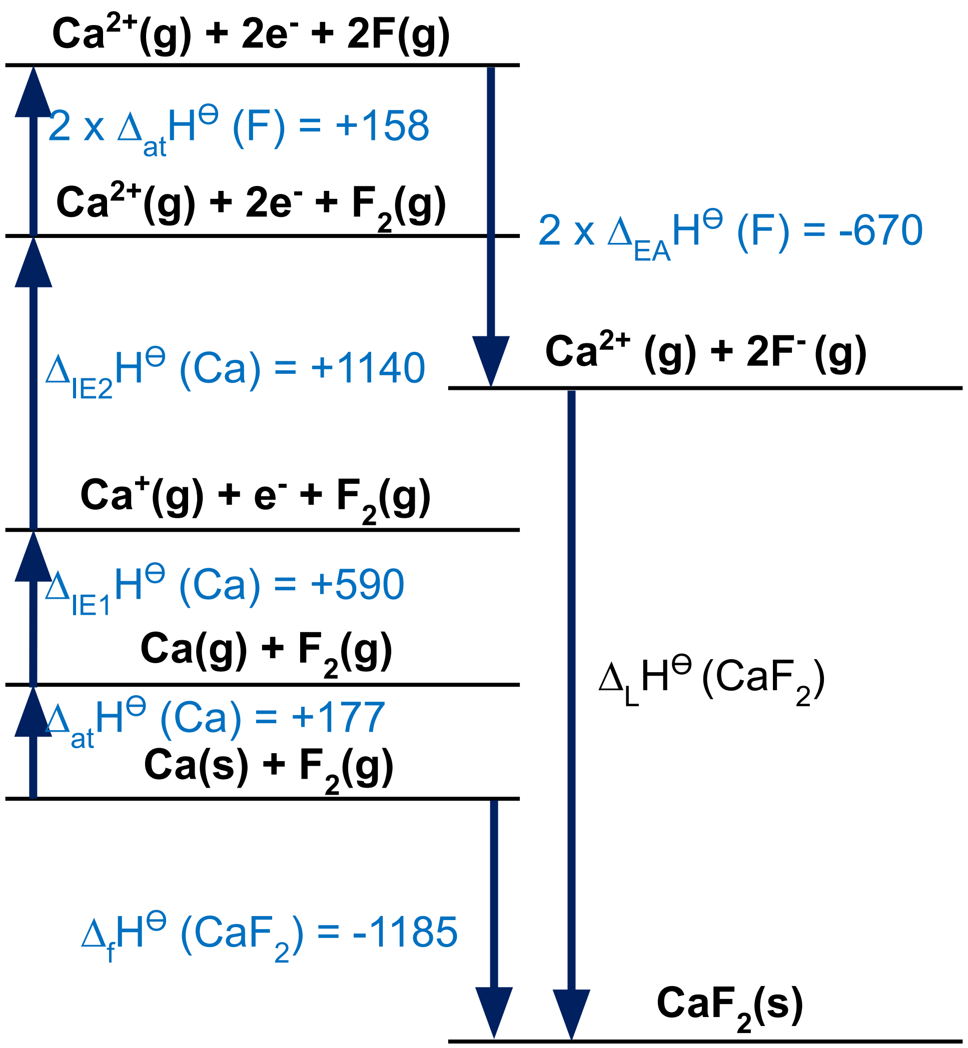
Enthalpy change of atomisation for fluorine	+79



1b) Using your completed diagram, calculate the lattice enthalpy of formation of calcium fluoride. **[2 marks]**

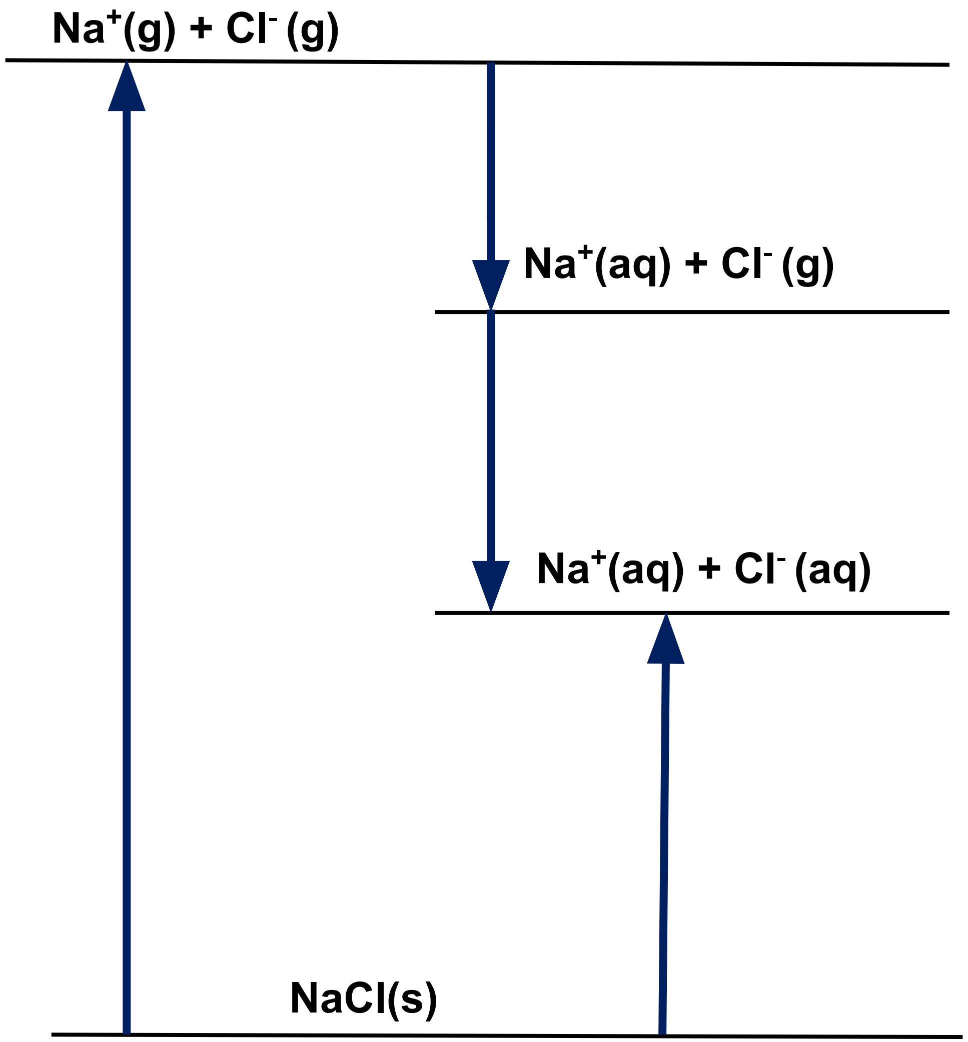
$\Delta_L H^\ominus (CaF_2) = -(-670) - (+158) - (+1140) - (+590) - (+177) + (-1185)$

$= \underline{-2580 \text{ kJ mol}^{-1}}$



2a) Complete and label the solvation enthalpy cycle for the solvation of sodium chloride using the data provided. **[4 marks]**

Process	Enthalpy change / kJ mol^{-1}
Lattice Enthalpy of NaCl	+788
Enthalpy of hydration of Cl^-	-406
Enthalpy of hydration of Na^+	-363



1b) Using your completed diagram, calculate enthalpy of solvation for sodium chloride.
[2 marks]